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(54) Title: DIRECT DEPOSITION OF PALLADIUM

(57) Abstract

The present invention is directed to a process for forming a layer of palladium on a substrate, comprising: preparing a solution of a palladium precursor, wherein the palladium precursor consists of $Pd(OOCR^1)_m(OOCR^2)_n$, wherein R^1 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbons substituted with one or two hydroxyl groups, R^2 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, –CHO, R^3 is alkyl, and alkyl groups from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, m and n are real numbers or fractions, and $m + n = 2$; applying the palladium precursor to the surface of the substrate; decomposing the palladium precursor by subjecting the precursor to heat.

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Direct Deposition of Palladium

The invention is directed to a process for directly depositing a layer of palladium on a substrate.

Palladium films act as excellent barrier layers for preventing migration of other metals in a substrate, such as an electrical contact, to the surface of the contact where oxidation of the other metal could take place. Palladium films are often made on a substrate by electroplating, vacuum sputtering, and laser direct-write metallization. Palladium is difficult to electroplate due to embrittlement on account of hydrogen induced cracking as the palladium is deposited. Palladium can also be deposited using electroless methods. Despite problems associated with electroplating and electroless methods, these processes are still used. Palladium films are best made by vacuum techniques such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), or sputtering.

In Gozum, et al. (Gozum, John E.; Pollina, Deborah M.; Jensen, James A.; Girolami, Gregory S. J. Am. Chem. Soc. 1988, 110, 2688), the chemical vapor deposition of a palladium layer is reported using bis(allyl)palladium, bis(2-methylallyl)palladium, and (cyclopentadienyl)(allyl)palladium as the starting precursor. The chemical vapor deposition of these precursors was accomplished at 250°C at 10^{-4} Torr. Palladium films were grown on substrates such as glass, steel, copper, and aluminum.

Gold can be deposited onto a substrate by decomposing a gold precursor. For example, in U.S. Patent No. 4,933,204, a method is shown for depositing gold features on a substrate. Gold(III) hydroxide is dissolved in acetic acid to form gold(III) acetate. Gold features were then formed by casting the gold(III) acetate film on a suitable substrate such as silicon,

and then traversing the film with a laser in the locations where it is desired to produce the conducting lines. The laser was operated at a power and speed sufficient to heat the traversed locations to a temperature above about 175°C. The gold(III) acetate was decomposed under the heat from the laser to release a layer of gold on the surface of the substrate and release the acetate.

What is needed is a milder method for depositing a layer of palladium on a substrate. What is further needed is a method which does not require the use of a vacuum for deposition, electroplating or electroless methods.

In one aspect, the present invention relates to a process for forming a layer of palladium on a substrate, comprising:

preparing a solution of a palladium precursor, wherein the palladium precursor consists of

$Pd(OOCR^1)_m(OOCR^2)_n$

wherein

R^1 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbons substituted with one or two hydroxyl groups,

R^2 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, -CHO,

R^3 is alkyl, and alkyl groups from 1 to 5 carbon atoms substituted with one or two hydroxyl groups

m and n are real numbers or fractions, and

$m + n = 2$;

applying the palladium precursor to the surface of the substrate;

decomposing the palladium precursor by subjecting the precursor to heat.

It is an object of the present invention to provide a non vacuum technique, non electroplating, and a non

electroless method for depositing a palladium film on a substrate.

It is a further object to provide a mild method for depositing a palladium film on electrical interconnects, flex circuits, multi-chip modules, and printed wiring boards.

It is a further object to provide an environmentally benign process releasing only benign compounds such as water and carbon dioxide into the environment.

As used herein:

"alkyl" refers to alkyl groups having from 1 to 10 carbon atoms , unless otherwise specified;

"alkenyl" refers to organic groups having 1 to 10 carbon atoms and at least one double bond, the unsaturation can be at any location;

"alkynyl" refers to organic groups having 1 to 10 carbon atoms and at least one triple bond.

It has been discovered that palladium(II) carboxylates, and in some cases, mixed palladium(II) carboxylates can be used as precursors to form a palladium film or layer on a substrate under very mild conditions. The palladium precursors that the film is prepared from have the formula:

$$Pd(OOCR^1)_m(OOCR^2)_n$$

where:

R^1 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbons substituted with one or two hydroxyl groups,

R^2 is hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, -CHO,

R^3 is alkyl, and alkyl groups from 1 to 5 carbon atoms substituted with one or two hydroxyl groups

m and n are real numbers or fractions, and $m + n = 2$.

More preferably, R^2 is hydrogen, alkyl of from 2 to 10 carbon atoms, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, and -CHO.

A few examples of the palladium precursors are:

$Pd(OOCCH_3)_m(OOCCH(C_2H_5)CH_2CH_2CH_2CH_3)_n$

$Pd(OOCCH_3)_m(OOCH)_n$

$Pd(OOCCH(C_2H_5)CH_2CH_2CH_2CH_3)_2$

$Pd(OOCH)_{1.5}(OOCCH(C_2H_5)CH_2CH_2CH_2CH_3)_{0.5}$

$Pd(OOCH)(OOCCH(C_2H_5)CH_2CH_2CH_2CH_3)$

$Pd(OOCCH(OH)CH(OH)COOH)_m$-
$(OOCCH(C_2H_5)CH_2CH_2CH_2CH_3)_n$

$Pd(OOCCH(OH)CH(OH)COOH)_2$

$Pd(OOCCHCH_2)_2$

$Pd(OOCCH_3)_m(OOCCHCH_2)_n$

$Pd(OOCCHCH_2)m(OOCCH_2OH)_n$

$Pd(C_2O_4)$

All of these compounds are capable of affording palladium films upon pyrolysis in air. These are mostly compounds with a mixed functionality and hence these afford good green films. These compounds are highly solvated in solution. Furthermore, upon pyrolysis, the compounds decompose to give environmentally benign byproducts.

The palladium precursors are formed in situ, within the solution which is to be applied to the substrate. Therefore, the exact ratio of the substituents is not determined. The compounds can be used directly without isolating and determining the ratio of the substituents. It is only important that the amount of palladium which is present in the solution is known.

The compounds have been prepared by mild solvolysis of palladium(II) acetate with the acids of the substituting anions in a polar solvent, such as ethyl acetate. Examples of methods to form metallo carboxylates are shown in U.S. Patent No. 5,021,398, which is herein incorporated by reference. The

palladium precursors are readily soluble in polar solvents such as methanol and DMSO. The palladium precursors can be applied directly to the surface of the substrate in these solvents for the formation of the palladium film. The choice of the particular palladium precursor to be used is dependent upon the substrate on which the palladium will be deposited.

The substrate onto which the palladium precursor can be deposited, and subsequently a palladium layer formed, can be a metallic material. Also, the substrate can be plastic, ceramic, glass, silicon wafer, cellulose, graphite, and paper substrates. Specific applications of this process can be used for placing a palladium layer on electrical contacts, multi-chip modules, printed wiring boards, and PCMCIA cards. This process presents an alternative to not only electroplating, but also to vacuum deposition techniques.

From the potential palladium precursors, the appropriate one may be chosen depending on the substrate to be used. For example, for the deposition of palladium on paper glyoxilic palladium glycoliate ($Pd(OOCCHO)_p(OOCCH_2OH)_q$) may be a better choice than others. This particular palladium compound will decompose slowly at 80°C, and very rapidly at 100°C. Therefore, this compound is suited for depositing palladium on paper because it decomposes at a low temperature. The thermal stability of the substrate is the governing factor in this consideration. For example, thermal analysis of palladium diglycolate shows that the compound decomposes at approximately 125°C. A good thermal analysis scan of glyoxilic palladium glycoliate could not be obtained because it was thermally unstable.

The palladium precursors can be applied to the substrate using a variety of different application techniques. The choice of a particular technique

depends on the end use and mode of production. The precursor can be applied using any one, or a combination, of the following techniques: ink-jet printing, screem printing, spray coating, spin coating, puddle coating, dip coating, brush coating, or various other coating techniques.

Surface pretreatment of the substrate is not absolutely necessary before applying the precursor, however, the palladium film adhesion to the substrate may be better if the surface is first activated by removal of grit, dust, grease and other contaminates, prior to application of the precursor solution.

In order to improve the film forming properties of the solution, a small amount of a non-ionic surfactant may be added to the solution of the palladium precursor. For example, TRITON X 100 (commercially available from Fluka Chemie AG) can be added to the solution of the precursor. Only a small amount of surfactant is added to the solution. For example, less than 0.1% by weight of the surfactant would be added to the solution of the palladium precursor. There are many other commercially available surfactants that can be used in the process. During pyrolysis of the palladium precursor, the surfactant will decompose. Alternatively, the surface of the substrate, following pyrolysis, can be washed with an organic solvent to remove any remaining organics or surfactants.

Furthermore, the surface of the substrate to be coated with the palladium precursor can be first treated with the non-ionic surfactant to allow better adhesion of the palladium layer to the substrate. As an alternative method, the surface of the substrate to be coated with the palladium precursor solution may be pretreated with a reducing agent, such as formic acid or vitamin C.

The precursor solution can be converted to a palladium film or layer by heating it to a temperature

above about 80°C, and in some cases above 100°C. The exact temperature necessary is dependent upon the precursor. Some precursors will decompose at a lower or higher temperature, depending on the substituents on the palladium. This can be accomplished by exposing the solution, in air, to a hot air gun, a laser, or a heat lamp.

The choice of a particular palladium precursor is dependent upon the substrate to which the palladium layer will be applied and how the substrate will stand up under a particular decomposition temperature. Glyoxilic palladium glycoliate is particularly well suited for application of a palladium layer onto sensitive substrates such as paper or plastic. Other substrates can withstand higher temperatures and therefore a laser could be used to decompose the palladium precursor. The length of time needed to decompose the palladium precursor will be dependent upon the palladium precursor and the power of the laser.

The process herein described could also be used to apply a palladium layer to a specific area of the substrate. To accomplish this, the surface of the substrate would be coated with the palladium precursor. The laser would then be directed toward particular parts of the substrate in order to decompose the palladium precursor on only those parts of the substrate. Once the decomposition of the specific areas of the palladium precursor was completed, the surface of the substrate would then be washed to remove any unreacted palladium precursor leaving a palladium layer in only those areas that were exposed to the laser.

After a first layer of palladium is deposited on the surface of the substrate, it is possible to apply subsequent layers of palladium to the surface by repeating the process. Furthermore, it is possible to apply a thicker coating of the palladium precursor to

the substrate in order to deposit a thicker layer of palladium to the substrate in one step.

Examples of methods used to form the palladium carboxylates and a palladium deposit from the film are given below.

Example 1

Preparation of glyoxilic palladium(II) glycoliate.

1.12 gm of palladium(II) acetate was placed in a flask and 20 ml methanol was added dropwise with stirring at room temperature. 0.38 gm of glycolic acid was added in small portions followed by addition of 0.47 gm of glyoxilic acid monohydrate. The contents were allowed to stir at room temperature for a total of 5 hours. After 1 hour, a clear blood red solution was obtained. The reaction was carried out in an argon atmosphere. The solution thus obtained is filtered through a micro filter to obtain a clear red solution. The filtrate was concentrated under a vacuum to 10 ml.

Example 2

Preparation of a palladium layer on nickel coated bronze paddles.

The paddles were coated with a solution glyoxilic palladium(II) glycoliate in methanol. The concentration of the solution was such that it had 12% w/w palladium in it. The substrate was allowed to air dry for a short period of time and then irradiated by a CO_2 cw laser, 10 watts, to generate the metal film.

Measurements were performed on the palladium layers on the nickel coated bronze paddles. Contact resistance measurements for two separate samples gave 2.56 and 3.29 milliohms respectively (load of 100g). Typical electroplated palladium has a contact resistance of 1.30 milliohms. The contact resistances of the samples are acceptable in the connector industry, even though they are somewhat higher than for the electroplated palladium. The measured values of coefficient of friction for both samples were in the range of 0.35 to

0.40 and are comparable to that expected for noble metal finishes used on separable contact interfaces. The samples also gave good wear testing after 100 cycles at 100 grams.

The preferred embodiments of this invention have been illustrated by the examples described above. Modifications and additional embodiments, however, will undoubtedly be apparent to those skilled in the art. Furthermore, equivalent elements may be substituted for those illustrated and described herein, and certain features of the invention may be utilized independently of other features. Consequently, the exemplary embodiments should be considered illustrative, rather than inclusive, while the appended claims are more indicative of the full scope of the invention.

What is Claimed is:

1. A process for forming a layer of palladium on a substrate, comprising:

preparing a solution of a palladium precursor, wherein the palladium precursor consists of

$Pd(OOCR^1)_m(OOCR^2)_n$

wherein

R^1 is taken from the group of hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbons substituted with one or two hydroxyl groups,

R^2 is taken from the group of hydrogen, alkyl, alkenyl, alkynyl, $-R^3COOH$, alkyl from 1 to 5 carbon atoms substituted with one or two hydroxyl groups, -CHO,

R^3 is taken from the group of alkyl, and alkyl groups from 1 to 5 carbon atoms substituted with one or two hydroxyl groups

m and n are real numbers or fractions, and

$m + n = 2$;

applying the palladium precursor to the surface of the substrate;

decomposing the palladium precursor by subjecting the precursor to heat.

2. The process of claim 1, wherein the palladium precursor is heated with a hot air gun.

3. The process of claim 1, wherein the palladium precursor is heated with a laser.

4. The process of claim 1, wherein the composition of the substrate is taken from the group of metal, plastic, glass, paper, silicon, graphite, and cellulose materials.

5. The process of claim 1, wherein a surfactant is added to the solution of the palladium precursor prior to application to the substrate.

6. The process of claim 1, wherein R^1 is -OOCCHO and R^2 is $-OOCCH_2OH$.

7. The process of claim 6, wherein the precursor is heated to about 80°C for decomposing the precursor.

INTERNATIONAL SEARCH REPORT

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PCT/US 98/03598

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C18/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4676796, LAPTEV V A ET AL: "Laser-assisted nickel deposition onto synthetic diamonds" XP002071652 see abstract & SYMPOSIUM C: ION BEAM, PLASMA, LASER, AND THERMALLY-STIMULATED DEPOSITION PROCESSES AT THE SPRING MEETING OF THE EUROPEAN MATERIALS RESEARCH SOCIETY CONFERENCE, STRASBOURG, FRANCE, 4-7 MAY 1993, vol. 241, no. 1-2, ISSN 0040-6090, THIN SOLID FILMS, 1 APRIL 1994, SWITZERLAND, pages 76-79, --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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A	DE 39 22 233 A (LINK GUENTER ;MORDIKE BARRY LESLIE (DE); BURCHARDS HANS DIETER (DE) 17 January 1991	

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3922233 A	17-01-1991	NONE	